Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–7

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Catalytic oxidative degradation of phenol using iron oxide promoted sulfonated-ZrO_2 by Advanced Oxidation Processes (AOPs)

Shailesh S. Sable[a], Kinjal J. Shah[a,b], Pen-Chi Chiang[a,b], Shang-Lien Lo[a,*]

[a] Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 10617, Taiwan
[b] Carbon Cycle Research Center, National Taiwan University, Taipei 10673, Taiwan

ARTICLE INFO

Article history:
Received 14 February 2018
Revised 21 June 2018
Accepted 22 June 2018
Available online xxx

Keywords:
Catalytic ozonation
Fe/sulfonated-ZrO_2
Fenton-like process
Mineralization
Phenol

ABSTRACT

In this paper, we report the efficiency of iron impregnated on both ZrO_2 and sulfonated-ZrO_2 catalysts for the catalytic oxidative degradation and mineralization of phenol (as a model organic pollutant) in the Fenton-like process and catalytic ozonation. Fe-impregnated on ZrO_2 and sulfonated-ZrO_2 catalysts were prepared, characterized, and used as an effective and reusable heterogeneous catalyst for the first time for phenol degradation and mineralization in both types of Advanced Oxidation Processes (AOPs). Among the studied catalysts, 4%Fe/sulfonated-ZrO_2 exhibited superior performance in ozonation, achieving a total conversion of phenol within 15 min and high mineralization efficiency of 88% in 6 h. And in Fenton-like process, achieving a total conversion of phenol in an hour and 64% of mineralization in 6 h. The sulfonation of zirconia followed by Fe impregnation has shown a positive effect on oxidative degradation and mineralization of phenol. The catalyst sustained its activity even after four cycles of regeneration and reuse. Overall, the present study offers Fe/sulfonated-ZrO_2 as an attractive catalytic material with high activity and stability for the abatement of phenol.

1. Introduction

Various organic pollutants discharged into the aquatic environment has become a great concern in recent years [1,2]. Several organic contaminants frequently found in wastewaters are unaffected by regular degradation and toxic to animal and human beings. Mostly, recalcitrant organic contaminants are hazardous and not destroyed by biological degradation [3]. Phenol and phenolic compounds are important toxic wastes, which polluted water resources. Therefore, the complete degradation and mineralization of these phenolic compounds become an interesting task for researchers [4]. Phenol and substituted phenols are one of the most active wastewaters discharged from various industries such as refineries, pharmaceutical, pesticides, insecticides, textile, and petroleum industry [5]. These phenolic compounds are very toxic and harmful for human health. The absorption of these phenolic compounds in the human body is rooted to several health problems such as impairment of pancreas, liver, and kidney and also it could be the reason for paralysis of the central nervous system [6,7]. Moreover, phenol is an important intermediate for many industrial products and because of these features, it has been studied extensively by many researchers in water and wastewater treatment [8–12]. Phenol-containing wastewater must be treated before being discharged into the environment, and this will prevent depreciation of quality of water and moderate the hazards posed to public health [13,14]. Therefore, it is important to the development of catalytic materials and effective process for the complete removal of these recalcitrant organic contaminants from water.

Advanced Oxidation Processes (AOPs) are generally characterized by the generation of hydroxyl radicals which are considered as a strong oxidant. Hydroxyl radical with high oxidation potential is able to oxidize and mineralize almost every organic molecule into CO_2 and inorganic ions. The development of new oxidation processes combined with catalysts that allow the complete destruction of phenolic compounds at the point of generation are needed [15,16]. AOPs such as ozonation and Fenton-like process have been extensively applied in many industries for wastewater treatment. Ozonation is used widely in water treatment but in some cases, it has been reported that there is difficulty in achieving complete degradation of organic contaminants and generate more poisonous intermediates [17,18]. Ozone-based AOPs such as catalytic ozonation are considered as effective techniques for water purification [19–23]. Several catalysts have been described in the literature showing excellent performance on the removal of organic pollutants. For example, metal oxides containing transition metals such as copper, nickel, iron, cobalt, silver, and magnesium have shown

* Corresponding author.
E-mail address: sllo@ntu.edu.tw (S.-L. Lo).

https://doi.org/10.1016/j.jtice.2018.06.030
1876-1070/

superior degradation of organic pollutants and improved TOC removal in catalytic ozonation [24–28]. Removal of phenolic and pharmaceutical contaminants by catalytic AOPs using platinum-based catalysts, hydrotalcites, FeOOH, and copper based-catalysts, magnetite (Fe_2O_3) nanoparticle and MgO nanoparticle in catalytic ozonation have been reported [29–34]. Application of catalysts in ozonation process has been received an attention when studied by Chen et al. [35] for phenol and ethyl acetoacetate removal using a Fe_2O_3 catalyst in a packed column with ozone. The Fenton process (dissolved $Fe^{2+} + H_2O_2$) is one of the most efficient processes to remove toxic organic pollutants present in the wastewater and has been proven as an economical technique [36,16]. Solid Fenton catalysts are more beneficial because of their application in handling, pH range and easy recovery when compared to homogeneous analogs [37]. Activated carbon, clays, resins or mesoporous materials, solid iron-oxide minerals or zero-valent iron and several solid supports such as zeolites have been studied for immobilization of iron species in heterogeneous Fenton-like processes [38–45]. Zirconia and iron-supported zirconia as heterogeneous catalysts have been used in catalytic and photocatalytic advanced oxidation processes [46–49]. Sulfated zirconia has been extensively applied in processes such as skeletal isomerization, alkylation, acylation, dehydration and esterification [50–54].

Among the above-mentioned catalysts, very few results have been reported on sulfated zirconia in catalytic advanced oxidation processes. Recently, iron oxide promoted sulfated zirconia have been only studied in O_3/H_2O_2 oxidation process for acetic acid degradation and Fe–ZrO_2 bimetallic oxide have been used in the catalytic photo-Fenton process [55,56]. No work has been reported on iron impregnated on the sulfonated-ZrO_2 catalyst for phenol degradation and mineralization in ozonation and Fenton-like process. Therefore, the iron oxide-sulfonated-ZrO_2 catalyst may exhibit high activity in ozonation and in Fenton-like AOPs.

This research work aims to investigate the efficiency of Fe/ZrO_2 and Fe/sulfonated-ZrO_2 materials as a catalyst for the oxidative degradation and mineralization of phenol by Advanced Oxidation Processes (AOPs) such as ozonation and Fenton-like process at very mild reaction conditions. The efficiency of the system was evaluated based on the phenol degradation and changes in total organic carbon (TOC).

2. Materials and method

2.1. Reagents

Phenol (Sigma-Aldrich); commercial zirconia (ZrO_2) from Saint-Gobain; hydrogen peroxide (H_2O_2, 30%), $Fe_2(SO_4)_3$•$5H_2O$, $Fe(NO_3)_3$•$9H_2O$ from Panreac and high-performance liquid chromatography (HPLC) analysis reagents (Fisher) were commercial grade. All other analytical grades of chemicals were used during catalysis preparation without further purification. All aqueous solutions were prepared with a Millipore system (Millipore Corp., Bedford, MA, USA).

2.2. Catalyst preparation

Sulfonation of Zirconia:

10 g of zirconia was calcined at 550 °C. Sulfonation of this calcined zirconia was carried out using 1 N H_2SO_4. 5 g of zirconia was soaked in 75 mL of 1 N H_2SO_4 (15 mL/gm of solid) for 2 h, filtered and dried at 150 °C overnight. Further, the dried material was again calcined at 550 °C for 5 h [57].

Impregnation of Fe on zirconia and sulfonated zirconia:

4%Fe/sulfonated-ZrO_2 was prepared by wet impregnation method. 0.48 gm of iron–nitrate was impregnated on 3 g of sulfonated zirconia. Approximately 0.8 mL of water was used to impregnate the metal on a support. The product obtained was dried in an oven at 65 °C for 2 h and calcined at 550 °C.

Table 1
ICP characterization data of the catalysts.

Catalysts	Fe (Wt%)
4%Fe/ZrO_2 (550 °C)	4.3
4%Fe/sulfonated-ZrO_2(550 °C)	4.1

2.3. Catalyst characterization

The metal content of the Fe/ZrO_2 and Fe/sulfonated-ZrO_2 catalysts were performed by ICP-OES (SPECTRO-ARCOS FHS16). The bulk and surface properties of the catalysts were characterized by using several techniques including XRD (Bruker-AXS D8-Discover diffractometer) having a Cu Kα radiation (λ = 1.541 Å) and N_2 adsorption method (Micromeritics ASAP 2010). In the XRD analysis, the measurement was scanned in the 2Θ range of 5°–70°. The data were collected with an angular step of 0.05° at 3 s per step and sample rotation with a 0.02° receiving slit and a scintillation counter as a detector. While for the case of N_2 adsorption, samples were degasified at 120 °C for 12 h and the surface area was calculated by the BET method. An environmental scanning electron microscope (ESEM Hitachi S-570, Japan) was used to analyze the surface morphology of iron impregnated ZrO_2 and sulfonated-ZrO_2 catalysts.

2.4. Catalytic activity test

2.4.1. Fenton-like reaction

Heterogeneous Fenton-like experiments were conducted at ambient temperature.

The phenol oxidation experiments were performed in glass reactor (capacity-250 mL) with 0.1 g/L of phenol solution (100 mL), H_2O_2 (0.5 g/L) and 2 g/L of the catalyst at ambient conditions (25 °C and atmospheric pressure). Fenton-like reactions were performed for 6 h and samples were periodically withdrawn, and prior to HPLC analysis samples were quenched by few drops of sodium thiosulfate solution. High-performance liquid chromatography (HPLC-Shimadzu LC-2010 equipped with SPD-M10A Diode array UV–vis detector) with Varian OmniSpher C18 column at 254 nm wavelength was used to monitor phenol concentrations during experiments. A solution containing water and acetonitrile (40:60) was used as mobile phase. Total Organic Carbon (TOC) was measured by as Shimadzu 5000-A analyzer. H_2O_2 was semi-quantitatively measured by H_2O_2 indicator strips. All the experiments were performed under dark conditions.

2.4.2. Ozonation experiments

The ozonation reactions were performed in a 1.5 L glass reactor containing a 500 mL aqueous solution of phenol (0.1 g/L) at ambient conditions (25 ± 2 °C) and atmospheric pressure. 0.5 g/L of catalyst was introduced into the phenol solution with 1.2 g/h of ozone which was generated by flowing pure oxygen gas (40 L/h) by an ozone generator (ANSEROS COM-AD-02). The reaction samples were withdrawn periodically for HPLC and TOC analysis.

3. Results and discussion

3.1. Catalysts characterization

Metal content (Fe, weight%) of catalysts are shown in Table 1. Iron contents of Fe/ZrO_2 and Fe/sulfonated-ZrO_2 catalysts were 4.3% and 4.1%, respectively, indicating that the final Fe content is similar to the theoretical values based on complete

Please cite this article as: S.S. Sable et al., Catalytic oxidative degradation of phenol using iron oxide promoted sulfonated-ZrO_2 by Advanced Oxidation Processes (AOPs), Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.06.030